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COLLISIONAL ENERGY TRANSFER IN HIGHLY VIBRATIONALLY EXCITED MOL--ETC(U)

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Energy transfer, rotational relaxation, laser, hydrogen fluoride, deuterium fluoride, vibrational relaxation.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
Combining the techniques of direct excitation of overtone vibrations and time resolved spectroscopic detection permits detailed measurements of the vibrational and rotational relaxation of highly vibrationally excited molecules. Using this technique, we have measured vibrational and rotational relaxation in HF(v=3,4,5). By observing near-infrared fluorescence, we determine the self-relaxation probabilities for HF(v=3,4,5) to be 0.19, 0.47, and 0.97, respectively, and find that the rates decrease more rapidly with temperature in these high levels than for v=1. Using laser double resonance to probe		

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cont. individual rotational states, we find phenomenological rotational relaxation rate constants which decrease monotonically with rotational energy change in the vibrationally excited molecule.

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COLLISIONAL ENERGY TRANSFER IN HIGHLY VIBRATIONALLY EXCITED MOLECULES

(Contract No. N00014-79-C-0415)

1. Principal Investigator:

F. F. Crim
Assistant Professor
Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

2. Contract Description:

The aspect of this work funded by the Office of Naval Research is the direct measurement of rotational relaxation rates of highly vibrationally excited deuterium fluoride. We expect to uncover systematic trends related to the initial rotational level of the excited molecule and to discover the influence which vibrational excitation has on rotational relaxation processes.

3. Scientific Problem:

Little experimental information is available on rotational energy transfer processes in general, and virtually none exists on the behavior of rotations in highly vibrationally excited molecules. This study will provide some of the first detailed data on rotational relaxation of molecules with large amounts of vibrational energy. As discussed below, the preparation technique and final state analysis are highly specific, so that the resulting rates represent an average over only the thermal rotational and translational energy distribution of the ground vibrational state collision partners. The rates come from a direct (time resolved) measurement of the populations of individual rotational states. Excitation of different vibrational states provides information on the influence which vibrational excitation has on rotational relaxation rates. Our measurements will be valuable for comparison to inferential techniques, such as overtone vibration linewidth measurements, and as a test of promising theories based on modified forms of the sudden approximation. These experiments on important but as yet unexplored rotational relaxation in highly vibrationally excited molecules promise to produce unique, detailed data which extend our fundamental and practical understanding of energy transfer dynamics and test

theoretical models of these processes.

4. Scientific and Technical Approach:

The detailed measurements of this study require two essential experimental capabilities: (1) preparation of a single rotational state in highly vibrationally excited molecule and (2) temporally resolved detection of the populations of other rotational levels (as well as that of the initially excited level). We prepare the desired state by direct excitation of a molecule from its ground vibrational state to an overtone vibrational level using visible photons from a pulsed dye laser or near-infrared photons produced by stimulated Raman scattering of the dye laser pulse in hydrogen gas. Because this excitation scheme relies on small transition probabilities arising from anharmonic terms in the potential and non-linear terms in the dipole moment expansion, only a small fraction of the molecules are excited. We have demonstrated, however, that this is adequate for vibrational relaxation measurements on HF($v=3,4,5$). [Chem Phys. Letters 71,258 (1980) and J. Chem. Phys. (in press).] We are using a Nd:YAG/dye laser and find that excitation of DF is quite feasible with this source. The short pulse duration (~ 6 ns) of this laser is also essential to our measurements of the temporal evolution of individual rotational levels. The detection scheme employs laser resonance absorption to probe a single rotational state in the highly vibrationally excited molecule. The exciting laser pulse and infrared probing radiation from a continuous HF/DF laser propagate collinearly through a long (~ 1 m) cell where transient absorption of the probe radiation mirrors the temporal evolution of an individual rotational state. After the cell, the visible (preparation) beam and infrared (probe) beam are separated, and the intensity of the probe beam is recorded by a fast InAs infrared detector and transient digitizer. A multichannel analyzer and computer accomplish the requisite signal enhancement, and analysis of the signal amplitude and form provides relaxation rates. The exciting laser selects a single vibrational-rotational level, while the probe laser interrogates an individual state also. This excitation and detection specificity is an essential feature of the experiment which provides the detailed information desired.

Our program is directed toward developing the noted experimental capabilities through a series of necessary measurements leading to the goal of determining rotational relaxation rates in highly vibrationally excited DF. We are extending

our first double resonance measurements on the $v = 2$ level of HF to rotational levels of HF($v > 2$) (which requires finding new operational limits of our infrared laser). Having achieved the HF analog of the desired measurement on DF, we will convert our infrared laser to DF operation (a relatively straightforward task after working with high levels of HF) and perform double resonance measurements on the weaker excitation candidate DF.

5. Progress:

During the past year, we have measured the vibrational relaxation rate of HF($v = 3, 4, 5$) prepared by direct excitation of overtone vibrations and found that the relaxation probabilities are 0.19, 0.47, and 0.97, respectively. These data yield a scaling relationship of $v^{2.7}$ and test several trajectory calculations. (G. M. Jursich and F. F. Crim, J. Chem. Phys. (in press)). We find that vibrational relaxation is primarily by a single vibrational quantum process. These experiments also measure the temperature dependence of the relaxation rate in high vibrational levels and show that the probability falls somewhat more rapidly than for $v = 1$.

We have also used our double resonance technique to determine the rotational relaxation rate in HF($v = 2$) by probing the temporal evolution of the population of a level J for initial excitation of each of the levels below it. Thus far, we have monitored $J = 2 - 5$ populations in this way while pumping each of the lower levels. The rates appear to decrease monotonically with energy defect ΔE of the rotational transition in the initially excited molecule; they decrease by about a factor of four in going from $\Delta E = 60 \text{ cm}^{-1}$ to $\Delta E = 570 \text{ cm}^{-1}$, corresponding to rate constants decreasing from $\sim 60 \mu\text{s}^{-1} \text{ torr}^{-1}$ to $\sim 15 \mu\text{s}^{-1} \text{ torr}^{-1}$. Even at the larger energy defects the rate is about three times gas kinetic. At this level of analysis, these rate constants are phenomenological quantities, $(P\tau)^{-1}$, and must be more thoroughly analyzed to provide level-to-level information. We are developing more sophisticated analysis and monitoring schemes as well as extending our measurements to higher vibrational levels.

6. Publications:

G. M. Jursich and F. F. Crim, "Vibrational Relaxation of HF($v = 3,4,5$)", J. Chem. Phys. (in press).

T. J. Foster and F. F. Crim, "The Temperature Dependence of HF($v = 3,4,5$) Energy Transfer Between 300 and 750 K", (in preparation).

R. A. Copeland, D. J. Pearson, and F. F. Crim, "Rotational Relaxation in HF($v = 2$)", (in preparation).

7. Extenuating circumstances:

None

8. No unspent funds will remain at the end of the contract period.

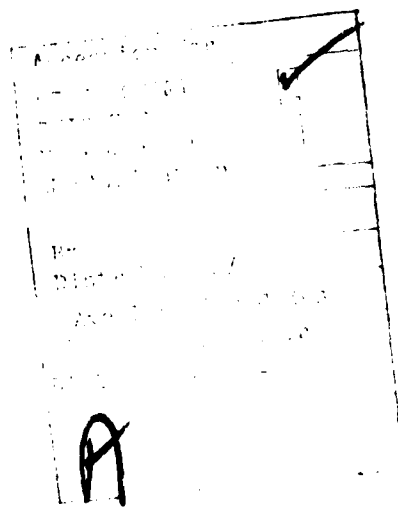
9. Two graduate students have received their degrees during this contract period.

T. J. Foster (MS)

B. D. Cannon (Ph.D.)

10. Other support:

Petroleum Research Fund	\$30,000	(2 years)
Department of Energy	55,000	(1 year)
Alfred P. Sloan Foundation	20,000	



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